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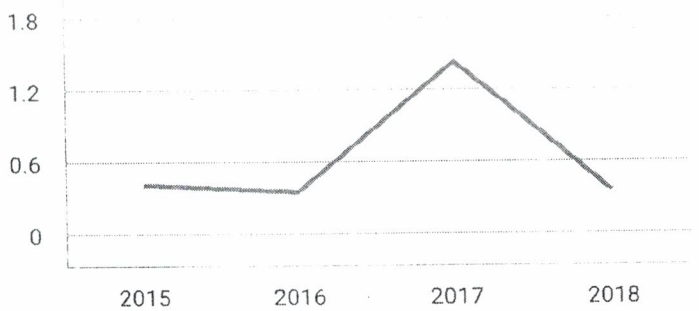

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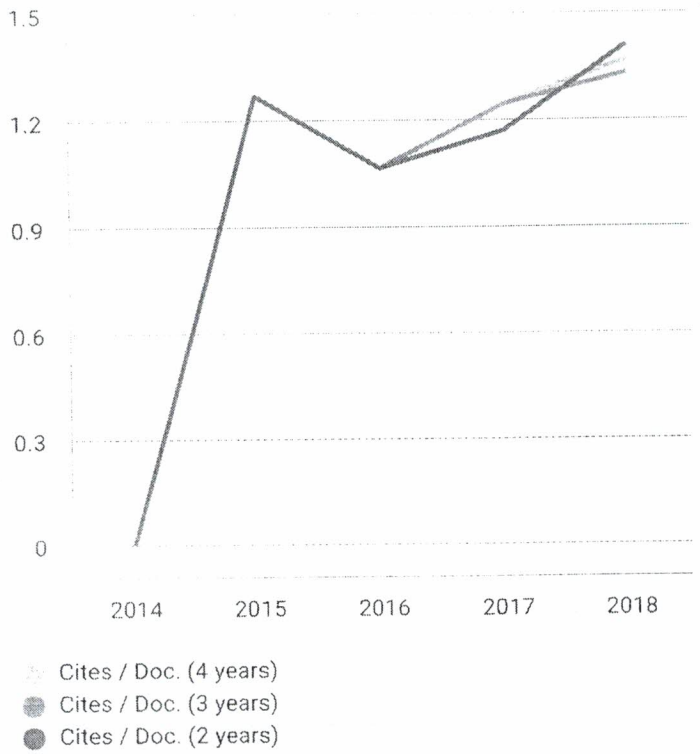

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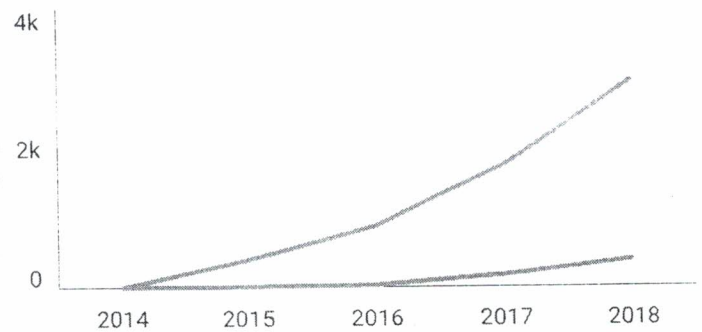

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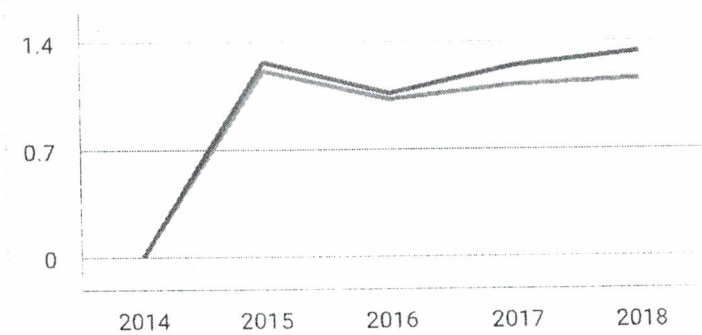

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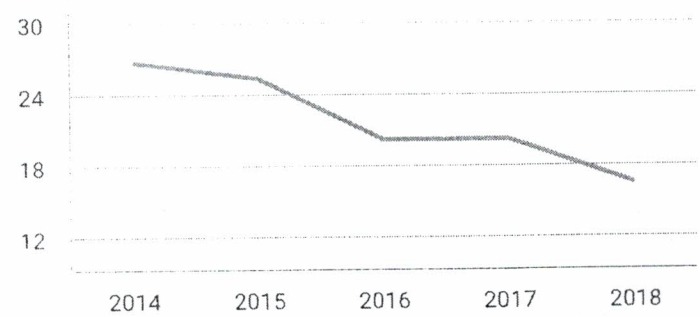

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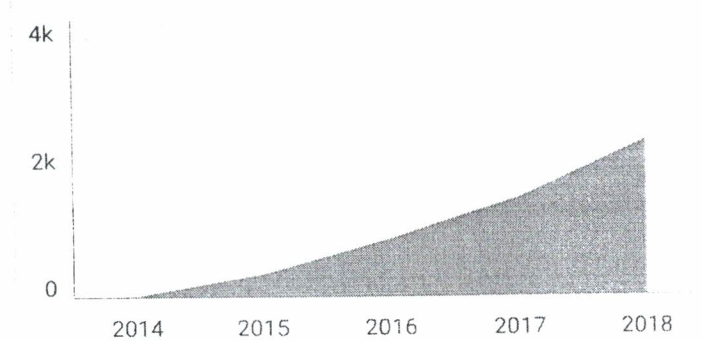

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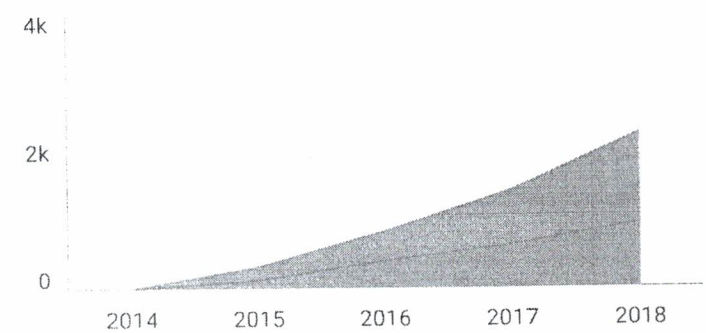

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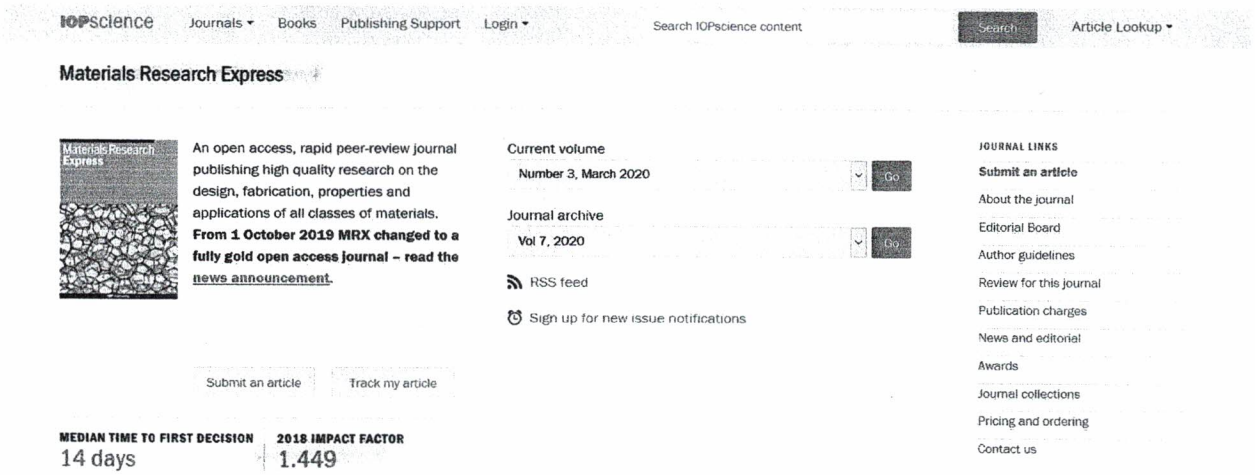

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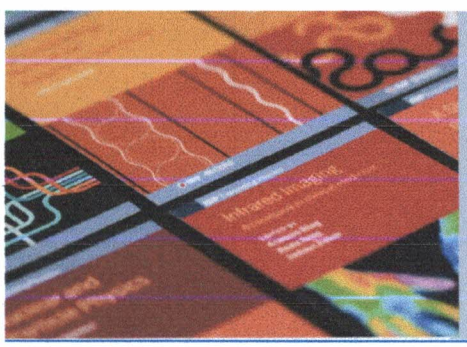

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PAPER

Adsorption of NO_2, HCN, HCHO and CO on pristine and amine functionalized boron nitride nanotubes by self-consistent charge density functional tight-binding method

Kriengkri Timsorn[1] and Chatchawal Wongchoosuk[2]

[1] Physics Division, Faculty of Science and Technology, Phetchabun Rajabhat University, Phetchabun 67000, Thailand
[2] Department of Physics, Faculty of Science, Kasetsart University, Chatuchak, Bangkok 10900, Thailand

E-mail: chatchawal.w@ku.ac.th

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Abstract

The adsorptions of toxic gases including NO_2, HCN, HCHO and CO molecules on the pristine and amine functionalized (5,0) single-wall boron nitride nanotubes (BNNTs) are investigated based on self-consistent charge density functional tight-binding (SCC-DFTB) method. The calculated results indicate that the pristine (5,0) BNNT exhibits weak adsorption for the gas molecules. Based on the calculated adsorption energy, interaction distances and charge transfer, amine functionalization at a boron atom of the pristine (5,0) BNNT enhances the sensitivity of the pristine (5,0) BNNT toward the gas molecules. The electronic densities of state results reveal that new local states in the vicinity of Fermi level for adsorption between amine functionalized BNNT and the gas molecules significantly appear. This confirms the improved sensitivity of the pristine (5,0) BNNT functionalized with amine for adsorption of the toxic gases. This study is expected to provide a useful guidance on gas sensing application of pristine and amine functionalized BNNTs for detection of the toxic gases at room temperature.

1. Introduction

Since boron nitride nanotubes (BNNTs) were first theoretically investigated in 1994 [1], they have attracted great attention both theoretical and experimental studies for different applications including gas sensors [2–6], drug delivery [7–9], gas storage [10–18] etc. The structures of BNNTs are similar to carbon nanotubes (CNTs) [2, 3] that exhibit remarkably electronic and mechanical properties, chemical stability [19, 20] and high thermal conductivity [21, 22]. The electronic properties of BNNTs are independent on their diameters and chirality [1, 2, 22]. Because of their uniquely electronic properties, BNNTs based gas sensors have been intensively theoretically studied for normal/toxic gas detection such as carbon monoxide (CO) [5, 23, 24], nitrogen dioxide (NO_2) [25, 26], hydrogen cyanide (HCN) [3, 4, 27], hydrogen gas (H_2) [28], oxygen (O_2) [29], and formaldehyde (HCHO) [2, 30]. Sensitivity and chemical reactivity of BNNTs to toxic gas molecules can be improved by doping metal atoms. For examples, Wang *et al* [2] studied the adsorption of formaldehyde molecule by pristine and silicon doped single-walled (8,0) BNNTs by performing density functional theory (DFT). The results showed that the silicon doped (8,0) BNNTs, regardless of boron or nitrogen atom doping of the BNNTs, exhibited higher sensitivity to formaldehyde than the pristine (8,0) BNNTs. Fan *et al* [19] reported that the adsorption of acetone on BNNTs was enhanced by doping transition metals (Al, Si, Cu, Co, Ni, Ga and Ge) on the BNNT surfaces. Zeng *et al* [4] investigated the performance of Al, Ni and Cu doped (8,0) BNNTs for adsorption of hydrogen cyanide using DFT. It was found that doping with these metals on the BNNTs can increase the adsorption of hydrogen cyanide. Xie Fan *et al* [5] studied adsorption of CO and NO gases on transition metals (V, Cr, Mn, Fe, Co, Ni) doped (8,0) boron nitride nanotube via PBE formulation. The transition metals could be used to tune magnetic moment and electronic structure of BNNT. Moreover, BNNTs with small diameters showed stronger interaction and higher sensitivity to toxic gases than those of BNNTs with bigger diameters

[3, 31]. Also, previous theoretical studies showed that the interaction between gas molecules and BNNTs doped with metals at boron atoms was stronger than N atom of the nanotubes [3, 32].

Covalent/noncovalent functionalization on BNNT surfaces can improve the electronic properties of BNNTs for gas sensor applications [22, 33–35]. The previous studies reported that the band structures of BNNTs may be changed by chemical functionalization [36, 37]. To the best of our knowledge, the reports about BNNTs functionalized with amine groups (NH_2) for adsorption of toxic gases are less available. Based on these motivations, we thus present the study of sensor performances of pristine (5,0) single-walled BNNT (pristine (5,0) BNNT) and amine functionalized (5,0) single-walled BNNT (NH_2-(5,0) BNNT) for adsorption of important dangerous NO_2, HCN, HCHO and CO gases using self-consistent charge density functional tight-binding (SCC-DFTB) method including van der Waals dispersion corrections. These gas molecules are chosen because they are the most common air pollutants that usually cause harm to human health and ecosystem. The air pollutions are generated from car engines, factories, power plants, human activity and natural processes [38, 39], i.e., typical internal car combustion engine produces high concentrations of CO when fuels burn incompletely. Internal combustion engines and the use of gas stoves for cooking also produce NO_2. The HCN is released from combustion of organic matter, building fires, cigarettes or car exhaust fumes while HCHO is found from furniture, cosmetics, cleaning products, glues, paints as well as contaminants in seafood [40]. Therefore, new sensing materials for detection of these air pollutions are still important. The results of this study are attributed to provide useful information and guidance for gas sensor designs in future experiments.

2. Calculation method

The SCC-DFTB method is based on a second-order expansion of the DFT total energy expression in term of charge density variation with respect to a reference density [41–45]. The total energy of SCC-DFTB based on the Kohn–Sham orbitals is given by following equation [44]:

$$E_{SCC-DFTB} = \sum_i \langle \phi_i | \hat{H}_0 | \phi_i \rangle + \frac{1}{2} \sum_{A,B} \gamma_{AB} \Delta q_A \Delta q_B + E_{rep} \quad (1)$$

where ϕ_i are the Kohn–Sham orbitals, $\hat{H}_0$ is unperturbed Hamiltonian, Δq_A and Δq_B indicate the induced charges of atoms A and B relative to the number of valence electrons, γ_{AB} is the second derivative with respect to its total charges and E_{rep} denotes two-body repulsive potential.

It should be noted that the benchmark of the SCC-DFTB calculation was systematically investigated with first principles DFT methods such as local-spin density approximation (LSDA), PBE, and hybrid exchange B3LYP DFT flavors [46]. The SCC-DFTB provided the molecular structures, energies and electronic properties in excellent agreement with DFT methods but was ~100–1000 times faster. The SCC-DFTB can also include reliable description of dispersions and weak interactions (Van der Waals and H-bonding) that are important roles for investigation of gas adsorption on a sensing material which is consistent with experimental observations [40, 45, 47, 48]. Moreover, the SCC-DFTB was proved to be effective in the simulation studies of boron nitride nanostructures systems [49–51].

In this study, structural optimizations and electronic properties of pristine and NH_2-(5,0) BNNTs with and without adsorption of NO_2, HCN, HCHO and CO gas molecules were investigated by using SCC-DFTB method. For amine functionalization on the surface of pristine (5,0) BNNT, the nitrogen atom of amine molecule was bonded with a boron atom of the pristine (5,0) BNNT. The pristine and NH_2-(5,0) BNNTs with length of 21.30 Å and diameter of 3.91 Å include 110 and 113 atoms, respectively. The BNNTs were saturated with hydrogen atoms at both ends to reduce boundary effects [19, 40, 52]. The matsci-0-3 parameter set for O-N-C-B-H system was employed for calculations. The parameter set supplies two center Hamiltonian matrix elements and two-body repulsive interactions [53]. It should be noted that the matsci-0-3 parameter set is well to describe BN interactions with small organic molecules containing oxygen, nitrogen, carbon and hydrogen [54–56]. The adsorption energy (E_{ad}) of pristine and NH_2-(5,0) BNNTs with gas molecules is calculated according to the equation:

$$E_{ad} = E_{tot}(\text{BNNTs + gas molecules}) - E_{tot}(\text{BNNTs}) - E_{tot}(\text{gas molecules}) \quad (2)$$

where E_{tot} (BNNTs + gas molecules) is total energy of pristine or NH_2-(5,0) BNNTs with gas molecules, E_{tot} (BNNTs) and E_{tot} (gas molecules) are total energies of pristine or NH_2-(5,0) BNNTs and gas molecules, respectively.

To find the most favorable adsorption sites of pristine and NH_2-(5,0) BNNTs, gas molecules were placed at different distances and orientation configurations (vertical and parallel positions) above the BNNT surfaces. All atoms of each gas molecule were pointed out into the boron (B) or nitrogen (N) atoms of the BNNTs. The adsorption of gas molecules on pristine and NH_2-(5,0) BNNTs surfaces can be classified into physisorption/chemisorption via the calculated adsorption energy. It should be noted that physisorption is characterized by

weak physical interaction (~10–100 meV) such as Van der Waals forces and hydrogen bonding while chemisorption involves a chemical reaction between the surface and the adsorbate with much stronger bonding bonds such as covalent bonding, strong electrostatic, and ionic bonding (>200 meV) [57–60]. For study of electronic charge transfer, the net charge transfer (Q) is defined as the charge difference between gas molecules adsorbed on the BNNT surfaces and isolated gas molecules [2, 61] and can be obtained by equation (3):

$$Q = Q(\text{BNNTs} + \text{gas molecules}) - Q(\text{gas molecules}) \quad (3)$$

where Q (BNNTs + gas molecules) and Q (gas molecules) represent the charges of gas molecules adsorbed on the BNNT surfaces and isolated gas molecules, respectively.

The energy gap (E_g) of the BNNTs is calculated using $E_g = |E_{LUMO} - E_{HOMO}|$, where E_{LUMO} and E_{HOMO} are the energy levels of the lowest unoccupied molecular orbital and the highest occupied molecular orbital, respectively.

3. Results and discussion

3.1. Structural and electronic properties of pristine and amine BNNTs

The pristine (5,0) BNNT was optimized to obtain the most stable structure as presented in figure 1(a). For the pristine (5,0) BNNT, bond lengths of a boron atom with its three neighboring nitrogen atoms; B-N1, B-N2 and B-N3 as shown in the inset of figure 1, were measured to be 1.536 Å, 1.537 Å and 1.537 Å, respectively. After amine functionalization at the boron atom, it was found that the local structure deformation at the boron atom functionalized with NH_2 molecule occurred. The boron atom of BNNT was slightly pulled out of the BNNT surface and its bond lengths with three surrounding nitrogen atoms were changed. The B-N_2 and B-N_3 were slightly elongated and found to be 1.578 Å. The B-N_1 was slightly shrunk with bond length of 1.487 Å. The bond lengths obtained in this study are in agreement with a previous study based on *ab initio* DFT calculations [33]. The result suggests that the covalent bond between the boron atom of BNNT and nitrogen atom of NH_2 molecule (bond length of 1.591 Å) is strong. This structural deformation is mainly due to the change in the local hybridization of the boron atom from sp^2 to sp^3 orbitals [22, 33, 62]. However, the overall structure of the nanotube after functionalization seems to be almost unchanged.

To study electronic properties, E_g, Fermi energy (E_F), E_{LUMO}, E_{HOMO} and electronic densities of state (DOSs) before and after functionalization were calculated as shown in table 1 and figure 1(b). After functionalization, a change in band structure was found. The energy gap increased from 1.37 eV to 1.65 eV. The increased energy gap indicates that $\pi - \pi^*$ band crossing of the pristine (5,0) BNNT is disturbed by NH_2 sidewall functionalization [34, 35]. The band gap slightly opens up between the conduction and valence bands. This effect is attributed to the breaking of the nanotube mirror symmetry due to the strong interaction between the BNNTs and NH_2 molecule [20, 34, 35]. Figure 1(b) shows DOS of pristine and NH_2-(5,0) BNNTs. By comparison with the DOS of the nanotubes before and after amine functionalization, it can be obviously seen that the increased DOS of NH_2-(5,0) BNNT appears below the vicinity of the Fermi level from −2.4 eV to −0.3 eV. This is considered that NH_2 moiety acts as acceptor impurity because of sp^3 hybridization between NH_2 molecule and the nanotube which induces an impurity state near the Fermi level [35]. In addition, DOS curve behavior of BNNT after amine functionalization is shifted to lower energies. It can indicate that the structure is more stable [63].

3.2. Adsorption of NO_2, HCN, HCHO and CO on the pristine (5,0) BNNT

To analyze adsorption performance of the pristine (5,0) BNNT to toxic gases including NO_2, HCN, HCHO and CO, the different adsorption structures were constructed and optimized. Some optimized structures for the most favorable adsorption sites are shown in figure 2. The typical calculated adsorption parameters are presented in table 2.

For NO_2 adsorption, N and O atoms of NO_2 molecule close to B or N atoms of the pristine (5,0) BNNT as displayed in figure 2(a). The calculated values of E_{ad} at N-N, N-O, B-N and B-O adsorption sites were −132.9, −77.7, −79.9 and −144.3 meV, respectively. The corresponding interaction distances were found to be 1.57, 2.11, 1.00 and 1.50 Å, respectively. Negative values of E_{ad} show that adsorption of NO_2 molecule on the pristine (5,0) BNNT is exothermic [2, 3]. Charge transferred from the pristine (5,0) BNNT to NO_2 molecule was only 0.0283 e, it indicates that NO_2 molecule undergoes weakly physical adsorption on the pristine (5,0) BNNT due to weak van der Waals interaction [2, 3, 24, 25]. The corresponding energy gap was calculated to be 1.96 eV which increased 0.59 eV than that of the pristine (5,0) BNNT. This suggests that conductivity of the pristine (5,0) BNNT after NO_2 adsorption decreases. Based on the results of table 2, the pristine (5,0) BNNT exhibits low sensitivity to NO_2 molecule, regardless of B or N atoms of the pristine (5,0) BNNT.

In case of HCN adsorption as presented in figure 2(b), according to table 2, the lowest value of E_{ad} was −106.4 meV at N-N and B-C adsorption sites with interaction distances of 1.59 and 1.50 Å, respectively. Unlike

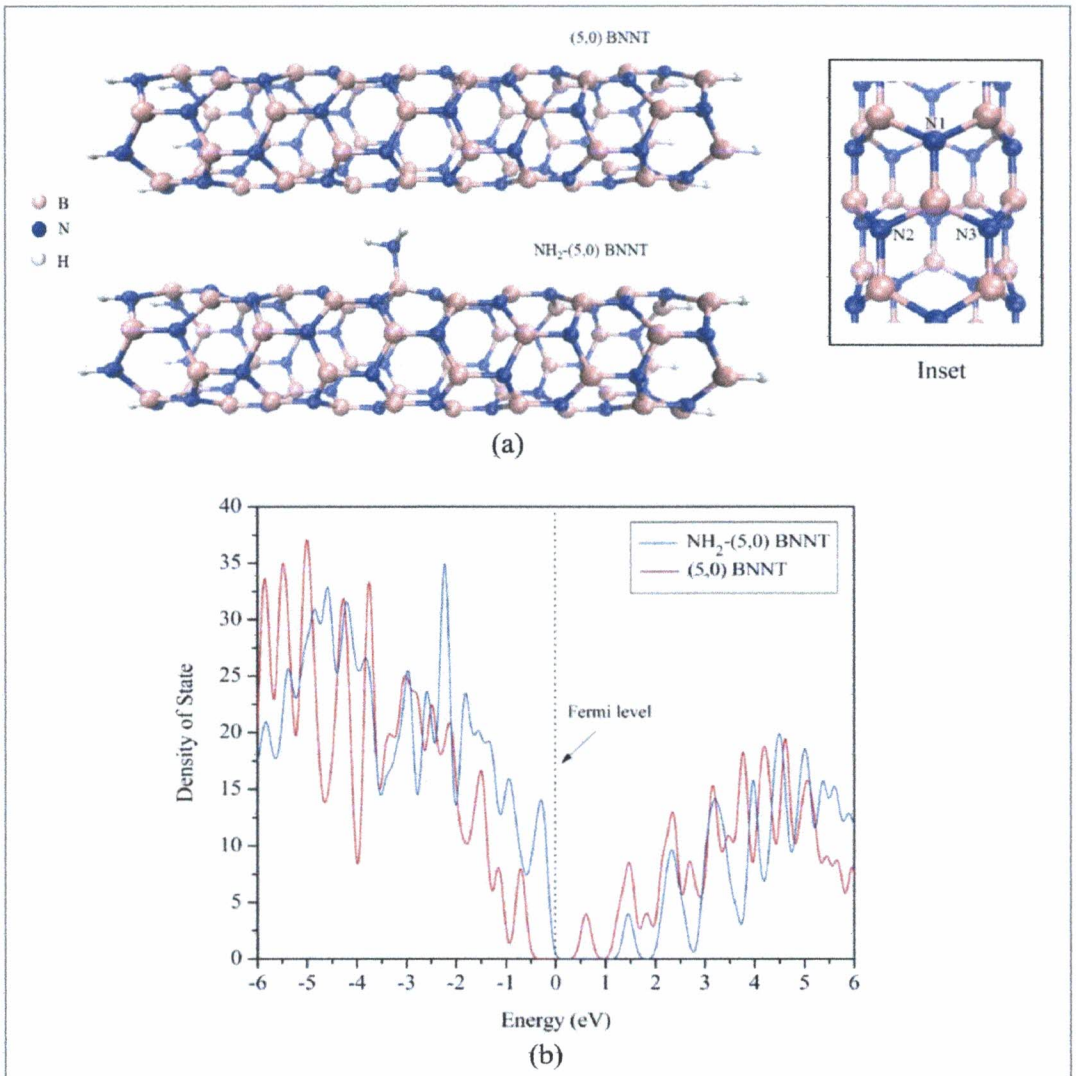

Figure 1. (a) The optimized structures of pristine and amine BNNTs and (b) total density of states of the nanotubes.

Table 1. Electronic parameters of (5,0) BNNTs before and after amine functionalization.

System	E_{HOMO} (eV)	E_{LUMO} (eV)	E_F (eV)	E_g (eV)
(5,0) BNNT	−6.19	−4.82	−5.46	1.37
NH_2-(5,0) BNNT	−6.30	−4.64	−6.13	1.65

other gases, HCN molecule prefers to adsorb on the pristine BNNT surface with parallel position. However, the charge transfer from HCN molecule to pristine (5,0) BNNT is quite small (~0.1 e). Interaction distances are smaller than 2.00 Å. The less negative E_{ad} value reveals a weak physical adsorption between HCN molecule and the pristine (5,0) BNNT [3, 4, 64]. This result is in agreement with [3, 4, 64, 65]. Looking at the calculated E_g, it was found that the E_g values at N-N and B-C adsorption sites fell to 1.12 eV. It means that adsorption of HCN molecule on the pristine (5,0) BNNT can improve conductivity of the nanotube. According to the results, the pristine (5,0) BNNT is little sensitive to HCN molecule.

For HCHO adsorption as shown in figure 2(c), we considered all adsorption sites including H, O and C atoms of HCHO molecule being close to B or N atoms of the pristine (5,0) BNNT, in vertical axis of HCHO

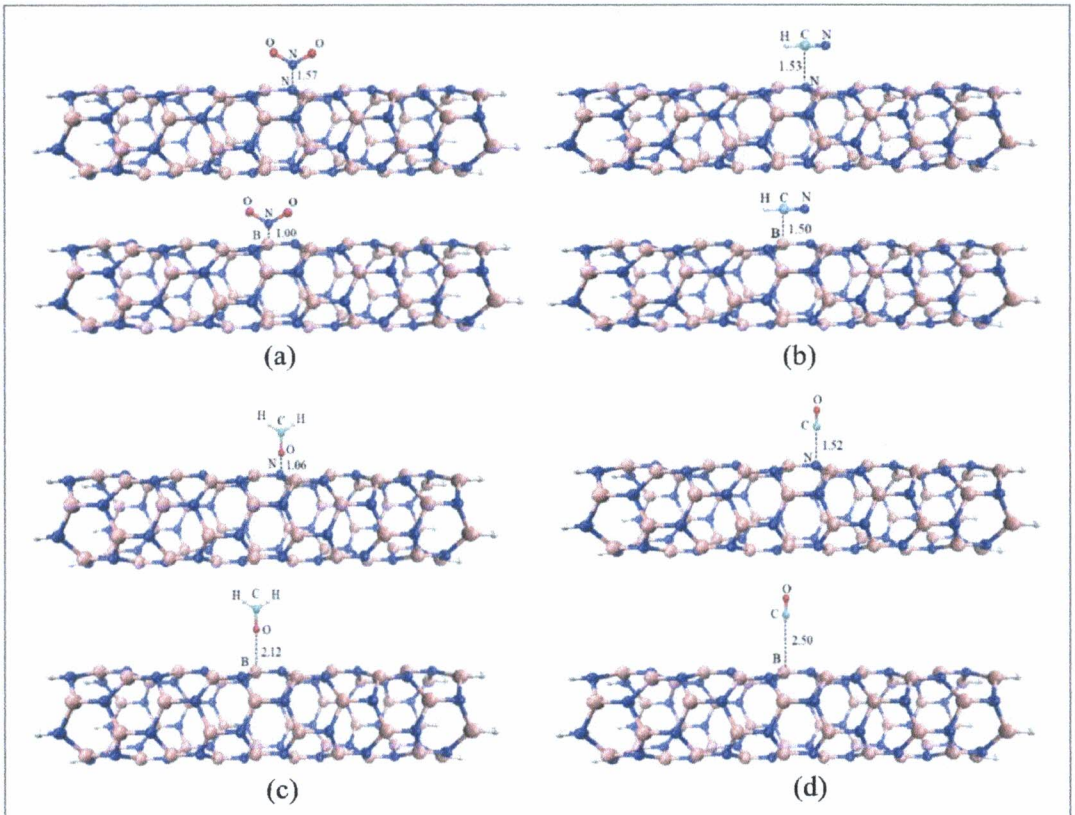

Figure 2. Some optimized structures for adsorption of the pristine (5,0) BNNT with (a) NO_2, (b) HCN, (c) HCHO and (d) CO gas molecules.

Table 2. Calculated adsorption parameters of target gas molecules absorbed on the pristine (5,0) BNNT.

System	Adsorption Site	Distance (Å)	E_{ad} (meV)	Q (e)	E_{HOMO} (eV)	E_{LUMO} (eV)	E_g (eV)
(5–0)-BNNT-N/NO_2	N–N	1.57	−132.9	−0.1807	−6.23	−4.75	1.48
	N–O	2.11	−77.7	−0.0283	−6.34	−4.38	1.96
(5–0)-BNNT-B/NO_2	B–N	1.00	−79.9	−0.0019	−5.95	−4.69	1.26
	B–O	1.50	−144.3	−0.0723	−6.12	−4.71	1.42
(5,0)-BNNT-N/HCN	N–N	1.59	−106.4	0.1075	−6.06	−4.94	1.12
	N–C	1.53	−81.9	0.0896	−6.38	−4.51	1.87
	N–H	2.00	−0.7	0.0003	−6.21	−4.80	1.41
(5,0)-BNNT-B/HCN	B–N	1.25	−9.8	0.0272	−6.04	−4.60	1.43
	B–C	1.50	−106.4	0.1075	−6.06	−4.94	1.12
	B–H	3.25	−0.8	0.0001	−6.22	−4.80	1.42
(5–0)-BNNT-N/HCHO	N–O	1.06	−168.2	0.0238	−6.26	−4.4	1.86
	N–C	2.00	−180.2	0.0907	−6.04	−4.97	1.07
	N–H	2.24	−55.6	0.0451	−6.08	−4.97	1.11
(5–0)-BNNT-B/HCHO	B–O	2.12	−52.7	0.0450	−5.95	−4.74	1.21
	B–C	2.00	3.4	0.0002	−6.23	−4.85	1.38
	B–H	2.53	−20.4	0.0261	−6.10	−4.67	1.43
(5–0)-BNNT-N/CO	N–C	1.52	−101.7	0.0516	−6.25	−4.83	1.42
	N–O	2.75	−1.6	0.0000	−6.19	−4.81	1.38
(5–0)-BNNT-B/CO	B–C	2.50	−58.8	0.0495	−6.04	−4.62	1.42
	B–O	1.64	−15.5	0.0392	−6.06	−4.64	1.42

molecule for H and O atoms and in parallel axis for C atom. The results showed that the most favorable adsorption site appeared at N-C adsorption site with the E_{ad} value of −180.2 meV. This result is consistent with [66] which reported that the most favorable adsorption site between HCHO and boron nitride sheet was found at C atom of HCHO interacting with N atom of the sheet. The corresponding charge transfer was calculated to be

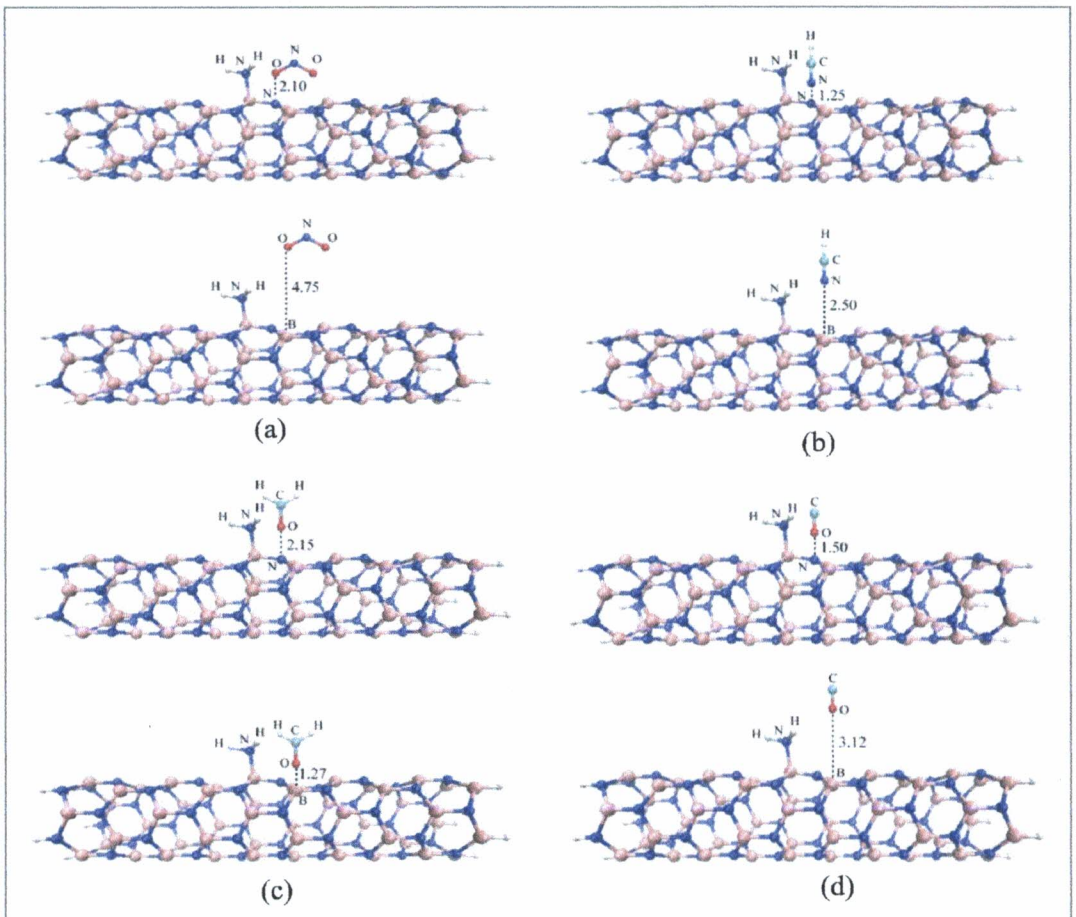

Figure 3. Some optimized structures for adsorption of the amine BNNT with (a) NO_2, (b) HCN, (c) HCHO and (d) CO gas molecules.

0.0907 e from HCHO molecule to the nanotube. This result suggests that the adsorption between HCHO (C atom site) and the pristine (5,0) BNNT (N atom site) results from an ionic bond interaction [66]. The ionic bonding plays an important role for charge transfer between the gas molecule and the BNNT. In this case, the ionic bond interaction is quite weak because of less charge transfer. As the results, the pristine (5,0) BNNT is weakly sensitive to HCHO molecule.

For CO adsorption, the C and O atoms of CO molecule in the vertical axis of CO molecule close to B or N atoms of the pristine (5,0) BNNT at different distances. The previous studies reported that CO adsorption on BNNTs in the perpendicular position to the BNNT axis was more stable than the parallel position to the BNNT axis [23, 67]. Figure 2(d) displays some optimized structures of the pristine (5,0) BNNT for CO adsorption. It is observed that the adsorption between CO molecule and the pristine (5,0) BNNT at C atom side of CO molecule is stronger than its O atom side. The calculated E_{ad} values at N-C and B-C adsorption sites were −101.7 and −58.8 meV, respectively. A change in energy gap of the nanotube by CO molecules was very less. Based on small E_{ad} values, large interaction distances and very small amount of charge transfer due to weakly physical interaction [68, 69], the pristine (5,0) BNNT is not sensitive to CO molecule.

3.3. Adsorption of NO_2, HCN, HCHO and CO on the amine BNNT

Figure 3 shows some optimized structures for the most favorable adsorption between the NH_2-(5,0) BNNT and NO_2, HCN, HCHO and CO gas molecules at different distances. Table 3 presents typical adsorption parameters of the NH_2-(5,0) BNNT with these gas molecules.

For NO_2 adsorption, the possible adsorption sites like NO_2-the pristine (5,0) BNNT system were investigated as shown in figure 3(a). It was found that the properties of the NH_2-(5,0) BNNT were significantly changed. At all adsorption sites, the E_{ad} values obviously increased in comparison with the pristine (5,0) BNNT. This demonstrates that the interaction between the NH_2-(5,0) BNNT with NO_2 molecule is stronger than the pristine (5,0) BNNT. The negative E_{ad} value indicates exothermic process of nature. Charge transferred from the

Table 3. Calculated adsorption parameters of target gas molecules absorbed on the amine BNNT.

System	Adsorption site	Distance (Å)	E_{ad} (meV)	Q (e)	E_{HOMO} (eV)	E_{LUMO} (eV)	E_g (eV)
NH_2-(5,0) BNNT/NO_2	N–N	4.11	−202.2	−0.3072	−6.16	−4.70	1.46
	N–O	2.10	−187.5	−0.2761	−6.15	−5.28	0.86
	B–N	3.05	−248.9	−0.3248	−6.07	−4.83	1.24
	B–O	4.75	−248.9	−0.3248	−6.07	−4.83	1.24
NH_2-(5,0) BNNT/HCN	N–N	1.25	−220.1	0.0825	−6.18	−4.32	1.86
	N–C	1.56	−196.1	0.1624	−6.26	−4.40	1.86
	N–H	2.00	−3.9	0.0378	−6.43	−4.68	1.75
	B–N	2.50	−30.7	0.2241	−6.37	−4.62	1.75
	B–C	1.73	−180.7	0.0352	−6.27	−4.45	1.81
	B–H	3.71	−3.9	0.0387	−6.43	−4.68	1.75
NH_2-(5,0) BNNT/HCHO	N–O	2.15	−230.7	0.0302	−6.52	−4.4	2.12
	N–C	1.91	−188.9	0.2702	−6.24	−4.39	1.85
	N–H	1.59	−50.4	0.0683	−5.34	−4.64	0.70
	B–O	1.27	−217.6	0.0883	−6.14	−4.40	1.74
	B–C	1.25	−113.5	0.1299	−6.02	−4.88	1.14
	B–H	2.80	−59.2	0.1977	−6.02	−5.25	0.77
NH_2-(5,0) BNNT/CO	N–C	1.15	−123.6	0.1185	−6.21	−4.72	1.49
	N–O	1.50	−77.0	0.1216	−6.22	−4.50	1.72
	B–C	1.85	−56.8	0.4986	−6.08	−4.48	1.60
	B–O	3.12	−2.2	−0.0001	−6.30	−4.64	1.66

NH_2-(5,0) BNNT to NO_2 molecule found at N-N adsorption site was 0.3072 e, which is higher than that of the pristine (5,0) BNNT. In case of energy gap, it dropped to 1.46 eV compared with 1.65 eV of the NH_2-(5,0) BNNT without NO_2 adsorption. This result reveals that the conductivity of the NH_2-(5,0) BNNT is improved by adsorption of NO_2 molecule. As the results, the sensitivity of pristine (5,0) BNNT to NO_2 molecule can be enhanced by amine functionalization.

For HCN adsorption on the NH_2-(5,0) BNNT, some optimized structures for adsorption are shown in figure 3(b). N and H atoms of HCN molecule were perpendicular to the nanotube surface and C atom was parallel to the nanotube surface. Based on table 3, the E_{ad} values for all adsorption sites are higher than that of HCN adsorbed on the pristine (5,0) BNNT. For example, the minimum E_{ad} value of the NH_2-(5,0) BNNT at N-N sites was −220.1 meV, which is about two times that of the pristine (5,0) BNNT. The previous studies reported that adsorption of HCN molecule with its N atom site interacting with BNNTs showed a stronger interaction than those of H and C atom sites [3, 27, 64]. The interaction distances between the nanotube and HCN molecule are also smaller than 2.00 Å. The previous studies calculated that the interaction distance between HCN molecules and metal doped BNNTs was about 2.00 Å [4, 70] which corresponds to this study. The calculated charge transfer shows that charge mostly transferred from the HCN molecule to the nanotube at B-N adsorption site. The maximum value reached to 0.2241 e. The charge transfer and E_{ad} value of HCN absorbed NH_2-(5,0) BNNT at B-N adsorption site are larger than that of the pristine BNNT, indicating that the orbitals of the nanotube and HCN molecule strongly overlap and charge clearly flows. This reveals that HCN molecule prefers N atom close to the NH_2-(5,0) BNNT at B atom. When HCN molecule interacted with the NH_2-(5,0) BNNT at either B or N atoms of the nanotube, it was found that energy gap increased. This demonstrates that the adsorption of HCN molecule changes band gap of the NH_2-(5,0) BNNT which belongs to chemisorption [4, 5]. From the results, functionalization of NH_2 molecule on pristine (5,0) BNNT improves both the strength of the interaction between HCN molecule and the nanotube and sensitivity of the nanotube to HCN molecule.

Figure 3(c) shows some optimized structures for adsorption between the NH_2-(5,0) BNNT and HCHO molecules. HCHO molecule prefers to adsorb on B or N atoms of the NH_2-(5,0) BNNT similar to the case of the pristine (5,0) BNNT. As listed in table 3, it was found that the trend of E_{ad} values of HCHO absorbed NH_2-(5,0) BNNT increased with the same range of interaction distance which indicates that the interaction is chemisorption [2, 69, 71]. The most charge transfer of HCHO absorbed pristine BNNT is positive which is charge transfer from HCHO molecule to the pristine BNNT similar to the NH_2-(5,0) BNNT. It was found that the charge transfer of HCHO absorbed NH_2-(5,0) BNNT was found at B-C adsorption site and reached to 0.1299 e. This result may be understood that NH_2-(5,0) BNNT is more accepting capability and ionic bond interaction between B atom of the nanotube and C atom of the gas molecule is enhanced which is consistent with a decrease in the E_g value from 1.65 eV to 1.14 eV. The results indicate that amine functionalization improves the sensitivity of the pristine (5,0) BNNT to HCHO molecule. Also, the same information was obtained at B-O site

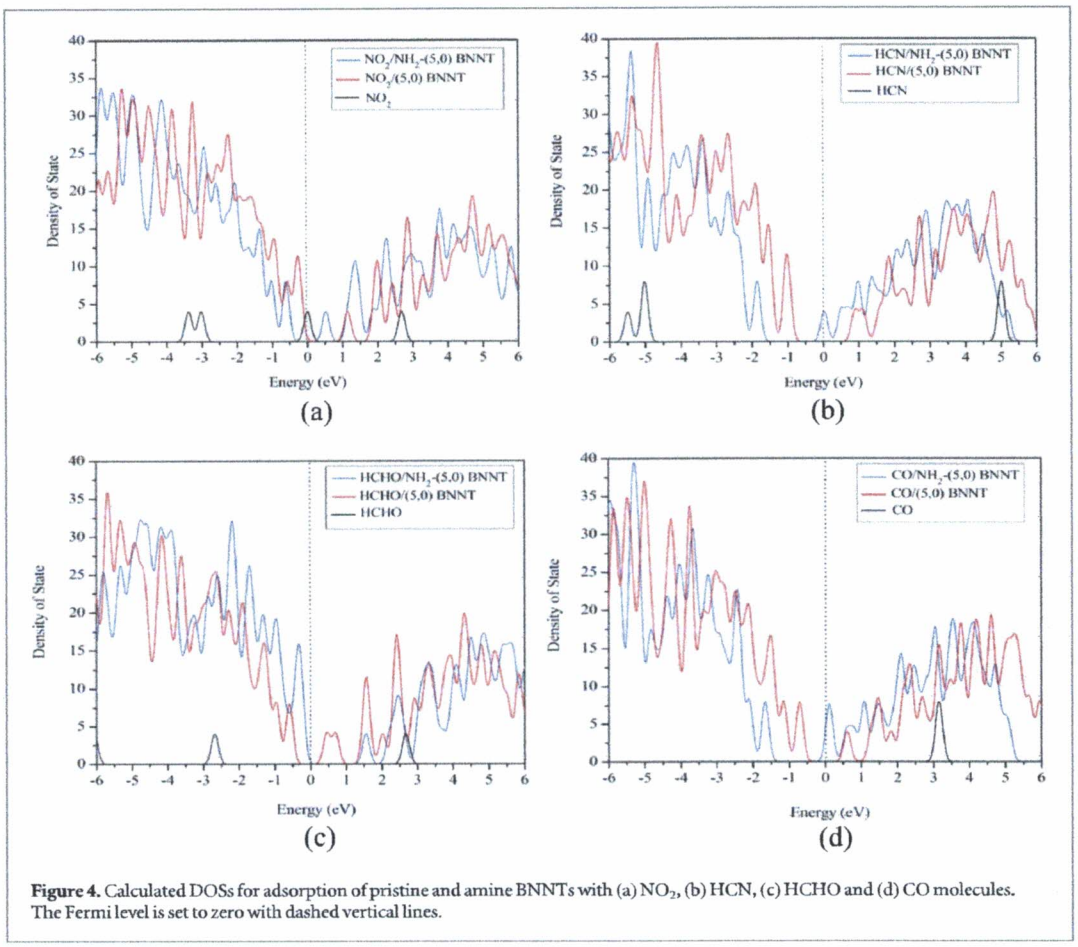

Figure 4. Calculated DOSs for adsorption of pristine and amine BNNTs with (a) NO_2, (b) HCN, (c) HCHO and (d) CO molecules. The Fermi level is set to zero with dashed vertical lines.

which confirms the improved sensitivity of the pristine (5,0) BNNT functionalized with NH_2 molecule to HCHO molecule. In addition, the results show a good agreement with previous studies [2, 66].

In case of CO adsorption on the NH_2-(5,0) BNNT, we also investigated the same adsorption sites with the pristine (5,0) BNNT and some optimized structures for adsorption between the NH_2-(5,0) BNNT and CO molecule are displayed in figure 3(d). After optimization, it was found that the E_{ad} values of CO absorbed NH_2-(5,0) BNNT at N-O and N-C adsorption sites obviously increased reaching to −77.0 meV and −123.6 meV, respectively. A decrease in interaction distances of the adsorption sites was found to be 1.50 Å and 1.15 Å, respectively. In case of pristine BNNT, charge transferred from CO molecule to the pristine BNNT at all adsorption sites. For NH_2-(5,0) BNNT, the most charge transfer from the CO molecule to NH_2-(5,0) BNNT was found to be at N-C adsorption site with value of 0.4986 e. As the results, it can conclude that amine functionalization on the pristine (5,0) BNNT enhances adsorption between CO molecule and the NH_2-(5,0) BNNT.

3.4. Electronic densities of state

To better understand the adsorptions between pristine, NH_2-(5,0) BNNTs and target gas molecules, electronic densities of state for these systems were calculated. Figure 4 shows the calculated DOSs of the most stable adsorption sites between the pristine, NH_2-(5,0) BNNTs and target gas molecules. It should be noted that the changes in DOSs in the area around Fermi level are expected that significant changes in electronic properties of the pristine and NH_2-(5,0) BNNTs for adsorption of target gas molecules are found. In figure 4(a), it can be seen that a new local state appears near the conduction band edge for NO_2/NH_2-(5,0) BNNT. This indicates that the NH_2-(5,0) BNNT exhibits a n-type semiconductor with donor impurity states for NO_2 adsorption [2]. This confirms the improved sensitivity of the NH_2-(5,0) BNNT to NO_2 molecule. In case of HCN adsorption with DOSs plot as shown in figure 4(b), a significant change in calculated DOSs for HCN/NH_2-(5,0) BNNT was observed. Two new local states appear near the Fermi level. One occurs on the top of valence band and the other one appears near edge of the conduction band compared with HCN/(5,0) BNNT. This suggests the existence of

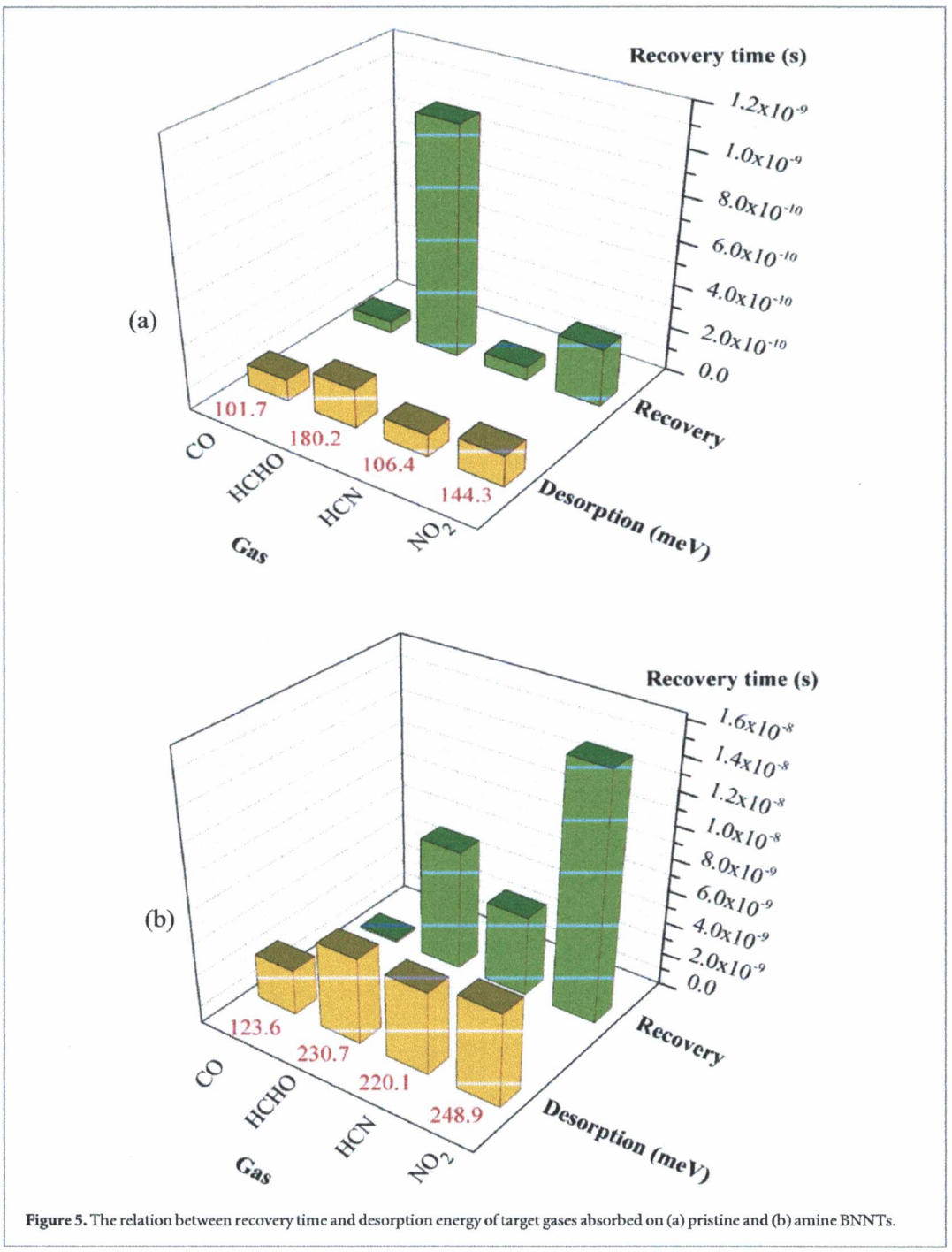

Figure 5. The relation between recovery time and desorption energy of target gases absorbed on (a) pristine and (b) amine BNNTs.

a new hybrid orbital between HCN molecule and NH_2-(5,0) BNNT [4] confirming higher sensitivity than HCN/(5,0) BNNT and the improved reactivity of the nanotube. For the calculated DOSs of HCHO adsorbed on the pristine and NH_2-(5,0) BNNTs as presented in figure 4(c), a new local state of the HCHO/NH_2-(5,0) BNNT occurs below Fermi level at −0.3 eV which corresponds to figure 1(b). This indicates that the NH_2-(5,0) BNNT is more sensitive to HCHO molecule than the pristine (5,0) BNNT. While calculated DOSs for the adsorption of the pristine and NH_2-(5,0) BNNTs with CO molecule are shown in figure 4(d). It was found that a new local state of CO/NH_2-(5,0) BNNT appears above the valence band compared with DOS of the CO/(5,0) BNNT. The DOS change suggests that the NH_2-(5,0) BNNT is more active toward CO molecule than the pristine (5,0) BNNT.

3.5. Recovery time and desorption energy

In this section, the relation between recovery time and desorption energy of pristine and NH_2 BNNTs was investigated at room temperature for its possibility as a gas sensor of target gas molecules. The strong interaction results in a long recovery time which suggests that the desorption process is difficult. The recovery time can be theoretically calculated based on transition state theory as the following equation [72, 73]:

$$\tau = \nu_0^{-1} \exp(-E_{ad}/kT) \quad (4)$$

where ν_0 is the attempt frequency ($\sim 10^{12}\ s^{-1}$ [72, 74]), T is temperature (300 K), and k is the Boltzmann's constant. As the equation, it is expected that more negative values of E_{ad} prolong the recovery time. To calculate desorption energy, E_{ad} value is equal to activation energy (E_a) which must be overcome in desorption process [74]. The desorption energy (E_d) can be predicted by assuming to be $-E_a$ [75]. This indicates that more negative E_{ad} values require higher desorption energy and long recovery times in desorption process. Figure 5 shows the relation between recovery time and desorption energies calculated from the most favorable adsorption sites of target gases absorbed on the pristine (5,0) and amine BNNTs. For the pristine (5,0) BNNT as presented in figure 5(a), the recovery time of NO_2, HCN, HCHO and CO molecules was found to be 2.64×10^{-10}, 6.11×10^{-11}, 1.05×10^{-9} and 5.10×10^{-11} s with the desorption energies of 144.3, 106.4, 180.2 and 101.7 meV, respectively. In case of the amine BNNT as shown in figure 5(b), the recovery time of NO_2, HCN, HCHO and CO molecules was calculated to be 1.51×10^{-8}, 4.95×10^{-9}, 7.46×10^{-9} and 1.19×10^{-10} s with the desorption energies of 248.9, 220.1, 230.7 and 123.6 meV, respectively. To compare results with other popular sensing materials, the recovery time of NO_2 desorption from the surface of carbon nanotube based gas sensors was found to be in the range of 5 μs to 16 s with corresponding to the adsorption energy range of -0.34 to -0.79 eV at room temperature [76]. Yong *et al* studied that the recovery times of NO and NO_2 on the graphitic GaN sheets were 1.1 μs and 0.16 ms, respectively [77]. Li *et al* reported that the recovery time of SnO_2 microspheres for a HCHO sensor was 25 s [78]. Therefore, it suggests that the NH_2-(5,0) BNNT has the good potential to act as a room temperature gas sensor with relative short recovery time.

4. Conclusion

In summary, we have studied the structural and electronic properties of the pristine and amine functionalized (5,0) BNNTs for adsorption of NO_2, HCN, HCHO and CO gas molecules using SCC-DFTB method. After amine functionalization, the structural and electronic properties of the pristine (5,0) BNNT were changed due to structural deformation from the change in local hybridization of the boron atom from sp^2 to sp^3 orbital. The calculated DOS of the NH_2-(5,0) BNNT below Fermi level increased. According to the adsorption results, the NH_2-(5,0) BNNT exhibits higher sensitivity to these gas molecules than that of the pristine (5,0) BNNT due to significant changes in band structure. For the adsorption of NO_2, HCN and CO molecules, it was found that new local states appear on and above the top of valence band in which a new local state of HCHO adsorbed on the NH_2-(5,0) BNNT occurs below Fermi level with increasing DOS. From the obtained results of recovery time and desorption energy, amine functionalized (5,0) BNNT at B atom of the nanotube can be used as reusable gas sensors for NO_2, HCN, HCHO and CO molecules at room temperature. The number of gas molecules adsorbed on pristine and amine functionalized BNNTs as well as dynamic properties will be deeply studied for future work. The results in this study are expected to be useful guidance for applications in gas sensor devices for detection of toxic gases.

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ORCID iDs

Chatchawal Wongchoosuk https://orcid.org/0000-0002-5613-6615

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